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EFFECT OF *IN-SITU* CURE ON MEASUREMENT OF GLASS TRANSITION TEMPERATURES IN HIGH-TEMPERATURE THERMOSETTING POLYMERS

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ABSTRACT

Using the dicyanate ester of bisphenol E (also known as Primaset LECy), we have illustrated the difficulties inherent in measurement of the glass transition temperature of this high-temperature thermosetting polymer via dynamic mechanical analysis alone. These difficulties result from the residual cure of samples heated beyond their glass transition temperatures. Comparative DSC and oscillatory TMA studies carried out using a variety of cure conditions showed that simply increasing the heating rate did not suppress the residual cure, although in many cases it allowed the glass transition to become apparent before the onset of rapid residual cure. The results indicated that ensuring the reliability of dynamic mechanical measurements of the glass transition temperature is very difficult to accomplish without the knowledge of residual cure properties provided by methods such as DSC.

1. INTRODUCTION

In the field of high-temperature thermosetting polymer resins, the glass transition temperature represents a critically important performance parameter. Typically, the maximum service temperature for a composite article is determined by subtracting an appropriate factor of safety from a measured value of the glass transition temperature. Above the maximum service temperature, the strength and stiffness of a polymer may decrease dramatically. Therefore, an unbiased and reasonably precise determination of the glass transition temperature of a thermosetting polymer is highly desirable. For thermosetting polymers with a very high glass transition temperature, generally above about 250 °C, however, accurate measurement of the glass transition temperature (T_G) can present a number of unexpected challenges. This paper illustrates the difficulties that can result from a lack of awareness of these challenges. It also describes specific strategies for obtaining accurate T_G measurements in high-temperature thermosetting polymers, utilizing cyanate ester resins as examples throughout.

In common practice, the glass transition temperature is determined by performing a dynamic mechanical analysis of a representative polymer or composite sample, according to a method such as ASTM E1640 [1]. Such methods typically encourage the use of very slow heating rates,

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often 1 °C per minute, as a way of avoiding uneven heating of the sample. However, at such low rates, the T_G values measured have been shown to differ by as much as 50 °C from the values measured using more reliable methods [2]. In previous work [3], it has been shown that the primary reason for this discrepancy is the tendency of thermosetting resins such as cyanate ester resins [4-6] to 1) reach less than complete cure when the maximum cure temperature is significantly below the T_G of the resin at full cure, and 2) to experience residual cure whenever heated beyond the maximum cure temperature. These two factors result in a T_G value that can increase during the course of a dynamic mechanical measurement. A dimensionless parameter describing the ratio of the rate at which the T_G can increase to the heating rate was proposed as a meaningful indicator of the reliability of dynamic mechanical measurements. This dimensionless parameter, equal to $S^*(d\alpha/dt)/(dT/dt)$, where S^* represents the sensitivity of the T_G to conversion, $d\alpha/dt$ is the rate of conversion, and dT/dt is the heating rate during the measurement, takes on unusually high values for cyanate ester resins, and will tend to be large for any resins that combine ease of processing with a high T_G at full cure.

Herein we refer to this dimensionless parameter as the T_G *instability number*, because a value of zero implies a perfectly stable T_G value that has no capacity to change during measurement, a value close to zero implies a negligible instability that may be ignored, and a large value implies a T_G value that is prone to change during measurement. It is important to note that the T_G instability number depends on temperature and conversion, and thus changes throughout the course of an experiment. As a result, it cannot be assumed that simply increasing the heating rate will decrease the T_G instability number, because in so doing, a different set of temperatures and conversion will be encountered, leading to a simultaneous change in the rate of conversion.

In this paper, we examine the relationships between heating rates and the instability of T_G in non-isothermal experiments intended to measure T_G . We utilize differential scanning calorimetry (DSC) to understand the kinetics of residual cure during non-isothermal experiments, and then utilize previously developed techniques [3,7] to compute the predicted dynamic behavior of the T_G with the aid of the diBenedetto equation [8]. We illustrate how dynamic mechanical experiments conducted under the same conditions are influenced, often in dramatic ways, by the instability of T_G . We further illustrate how factors such as cure temperature and catalysis affect the instability of T_G , again often in ways that are counter-intuitive. These examples lead to two important conclusions: 1) it is very difficult to prescribe a set of dynamic mechanical experimental conditions that will provide a reliable estimate of the “as cured” T_G of an undercured thermosetting polymer, and 2) for some types of thermosetting polymers, traditional mechanical spectroscopy alone cannot be utilized to measure T_G . In light of this conclusion, we discuss how the incorporation of chemical kinetics data through techniques such as DSC can be utilized to assess the reliability of “as cured” T_G measurements by mechanical spectroscopy.

2. EXPERIMENTATION

2.1 Materials

The dicyanate ester of Bisphenol E, that is, 1,1-bis(4-cyanoophenyl)ethane, also known commercially as Primaset LECy, was obtained from Lonza and stored at 5 °C. Nonylphenol (technical grade) was purchased from Aldrich, and Copper (II) acetylacetonate was purchased from ROC/RIC; both were used as received. Batches of catalyst comprised of 30 parts by weight nonylphenol to one part by weight of copper (II) acetylacetonate were prepared by mixing the

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ingredients in a vial and heating to 60°C while stirring vigorously until complete dissolution took place (typically one to two hours). These batches were retained for up to 30 days.

2.2 Sample Preparation

When preparing catalyzed samples, the previously prepared catalyst mixture was mixed with LECy at a weight ratio of 2 parts catalyst per hundred parts LECy. Batches of a few mL of LECy (either with and without added catalyst) were placed in a glass vial and de-gassed for 30 minutes under a partial vacuum of 300 mm Hg, then cast into silicone molds to form discs approximately 3 mm thick and 12 mm in diameter. The molds were prepared from R2364 room-temperature vulcanized silicone purchased from Silpak, Inc., by mixing 10 parts by weight of the supplied “A” component with 1 part by weight of the supplied “B” component, casting overnight, then post-curing at 150 °C for 1 hr, and, finally, de-gassing under at least 300 mm Hg of vacuum for one hour, just prior to casting. The discs were cured in the mold under nitrogen either for 12 hours at 150 °C, or for 1 hour at 150 °C followed by 24 hours at 210 °C, as indicated, using ramp rates of 5 °C / min. for all steps. Small pieces of these discs were broken off and placed in hermetic DSC pans for DSC analysis. The remainder of the discs were utilized for oscillatory TMA (dynamic mechanical) analysis.

2.3 Characterization

DSC was performed on a TA Instruments Q2000 calorimeter under 50 mL/min. of flowing nitrogen. Samples were heated at 10 °C / min. to 350 °C, cooled at 10 °C / min. to 100 °C and heated once again at 10 °C / min. to 350 °C. For each sample, a baseline was generated using an algorithm that starts with the re-scanned signal, applies an offset, adjusts for changes in T_G during residual cure, and accounts for degradation of the sample. A detailed explanation of the algorithm has been previously published [7]. Integration of the signal relative to the baseline was utilized, along with previously published information about the enthalpy of cure for catalyzed [7] and uncatalyzed [9] LECy, to determine the “as cured” conversion, including a measurement of uncertainty, also as described in a previous publication [7]. The DSC signal was then utilized to compute the instantaneous rate of change of conversion, and the rate values were integrated in order to estimate the conversion at every point in the first non-isothermal DSC scan, also according to previously published procedures [3,10]. The diBenedetto equation [8], along with previously published diBenedetto equation parameters for catalyzed LECy [11,12], were utilized to obtain an estimate of the T_G at every point in the DSC scan, also as described previously [3,10].

Oscillatory thermomechanical analysis (TMA) was performed on a TA Instruments Q400 in dynamic TMA mode. Samples were pre-loaded with a force of 0.2 N, then subjected to an oscillatory compressive stress of mean value 0.1 N, amplitude 0.1 N, and frequency of 0.05 Hz. The standard 5 mm flat cylindrical quartz probe was used for all measurements. All time-temperature protocols included at least two heating and cooling loops to determine thermal lag and a heating to 350 °C, but varied according to the heating rate applied. The variation was necessary in order to provide adequate thermal equilibration time without residual cure while measuring thermal lag. For catalyzed LECy cured at a maximum temperature of 150 °C and heated at 2 °C / min., the complete protocol consisted of two heating and cooling loops at 2 °C / min. between 0 °C and 100 °C, followed by heating at 2 °C / min. to 350 °C, cooling at 10 °C / min to 50 °C, and re-heating at 2 °C / min to 50 °C. Note that the temperatures reported for these

protocols are instrument set-points. For the analogous catalyzed LECy heated at 10 °C / min., the complete protocol consisted of two heating and cooling loops at 10 °C / min. between 0 °C and 100 °C, followed by heating to 350 °C, cooling to 50 °C, and re-heating to 350 °C, all at 10 °C / min. For the analogous sample at a 20 °C / min. heating rate, the complete protocol was initial heating to 350 °C, followed by two loops of cooling to 100 °C and heating to 200 °C, all at 20 °C / min. (this sample was not re-heated). For the analogous sample at 50 °C / min, the complete protocol was two loops of heating and cooling between -60 °C and 140 °C, followed by heating to 370 °C, cooling to 25 °C, and re-heating to 370 °C, all at 50 °C / min. The different set-points in this protocol are based on experience with the instrument control system, and are designed to ensure that the actual sample temperatures span the ranges seen using other heating rates. The actual cooling rates also tend to fall short of the 50 °C / min. change in set-point by a considerable amount (a typical maximum cooling rate of 30-35 °C / min. was achieved). This shortfall has the practical effect of ending the cooling run short of the minimum set-point temperature, thus necessitating the changes in set-point described earlier.

For catalyzed LECy cured to a maximum temperature of 210 °C, the complete protocol for samples heated at 10 °C / min. was an initial heating to 350 °C, followed by cooling to 100 °C, followed by two heating and cooling loops between 100 °C and 200 °C, and a re-heating to 350 °C, all at 10 °C / min. For the analogous sample heated at 20 °C / min, the complete protocol was an initial heating to 350 °C, followed by two heating and cooling loops between 100 °C and 200 °C, and a final heating to 350 °C, all at 20 °C / min. For the uncatalyzed LECy sample cured at a maximum temperature of 210 °C and heated at 50 °C / min, the complete protocol was two loops of heating and cooling between -50 °C and 200 °C, followed by heating to 350 °C, cooling to 350 °C, cooling to 100 °C, and re-heating to 350 °C, all at 50 °C / min.

The thermal lag for all samples was computed using the loops only, according to procedures reported previously [7], with the exception that for the 50 °C / min samples, the displacement used as the reference point in computing the lag was at the mid-point, rather than 25% of the distance from the minimum to the maximum. The use of this displacement ensured the linearity of the segments used in the computing the lag, and provided the maximum time for equilibration.

3. RESULTS

Figure 1 shows the DSC of catalyzed LECy after curing to 150 °C for 12 hours, using a 2 °C / min. heating rate. The residual cure is evident from the large exotherm seen in the first heating, spanning from about 180 °C to 320 °C. Just before the onset of cure, a glass transition is visible (note the similarity to the unobscured T_G seen in the second heating). The calculated conversion is 0.882 ± 0.013 , allowing for a 10% error in sample weight in addition to the baseline-based uncertainty described previously. The degradation of the LECy network appears pronounced above 300 °C, likely due to the slow heating rate being utilized. Not surprisingly, the “post-cured” T_G , at around 270 °C, is lower than the expected 290 °C [11,13], likely due to the degradation.

Figure 2 shows the computed conversion, conversion rate, and T_G during the scan. The T_G is computed using three cases in order to understand the inherent uncertainties. For LECy, the diBenedetto parameters T_{G0} , $T_{G\infty}$, and λ are all known, meaning that an expected T_G may be computed for any value of the conversion α . In this case, there are no adjustable parameters, but

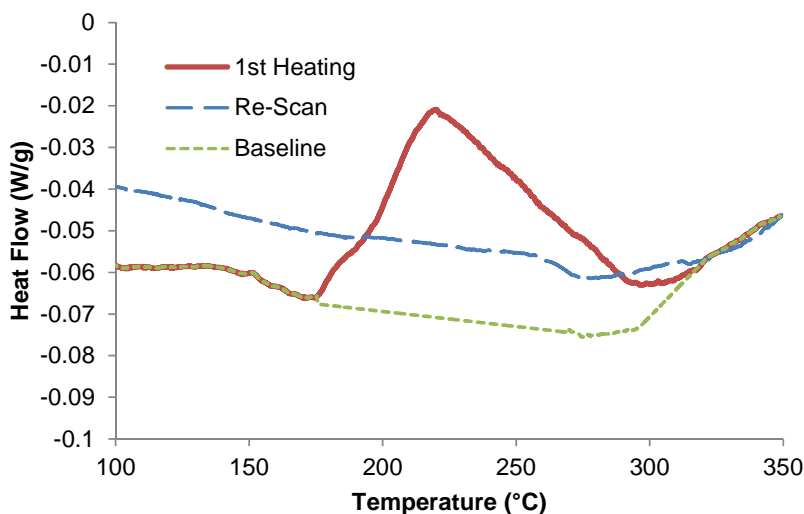


Figure 1. DSC scan of catalyzed LECy cured at 150 °C for 12 hours, then heated at 2 °C / min, showing original heating, re-scan, and baseline.

the use of all of these parameters ignores the very clear experimental measurement of a well-defined T_G value by DSC and produces instead a highly uncertain value for the “as-cured” T_G , an outcome that is far less desirable. Instead, we opted to use the known range of T_G values directly measured by DSC, and the known ranges of α , T_{G0} , and $T_{G\infty}$ to generate the curves, using the values of λ that best fit the initial T_G values. We also took into account the uncertainty in the offset between T_G values from DSC mid-points and OTMA loss peaks, which has been reported as 4 ± 9 °C [13] (positive values representing higher measured OTMA loss peak temperatures). For $T_{G\infty}$ (that is, the T_G at full cure), we assumed that the observed value in the DSC, which is affected by degradation, reflected the lowest possible $T_{G\infty}$ value, because such a value implies that all degradation happens before the end of the heating scan (even though the sample still experiences high temperatures for some period during cooling). We assumed that the highest value recorded for OTMA measurements made where degradation was confirmed to be minimal (296 °C) [2] represented the highest possible $T_{G\infty}$ value, because such a value implies that no degradation takes place until the scan reaches its maximum temperature. We then took the combination of α , $T_{G\infty}$, and DSC to OTMA T_G offset that gave maximum and minimum possible values for T_G during the scan, and plotted those “low” and “high” cases along with the “medium” case that includes the most probable value of α , no offset between DSC and OTMA T_G values, and the previously reported value of $T_{G\infty}$. Together, these cases illustrate the range of possible T_G values present during the scan. These can be compared to the scan temperature with the aid of the diagonal line in the Figure.

For LECy, the value of S^* is about 900 °C, based on the diBenedetto parameters [11]. With a maximum cure rate around 0.2 / h (0.003 / min.), the T_G instability number is around 1.5, indicating that the T_G could increase somewhat faster than the heating rate. According to Figure 2, the T_G does increase faster than the heating rate, a feature that can easily be discerned by noting that the slopes of the lines that trace T_G are higher than that of the diagonal line. In the “high” case, the T_G and the scan temperature intersect at three different points during the scan. These intersections indicate points where a T_G should be observed by OTMA. (Table 1 provides

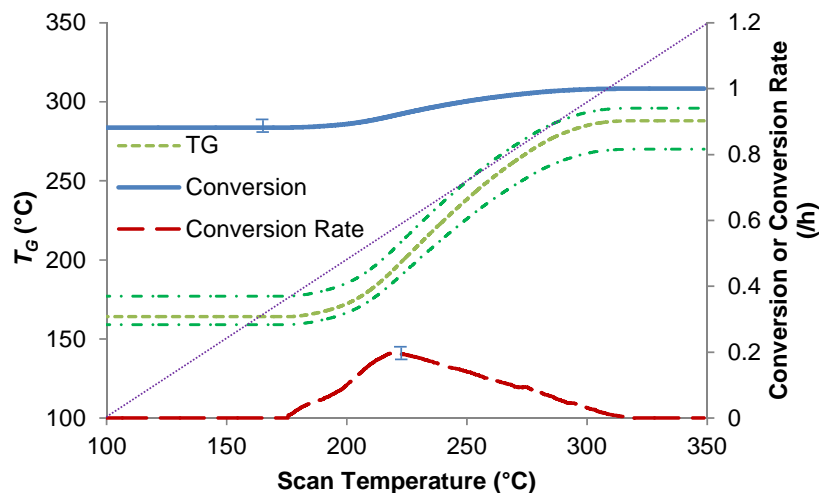


Figure 2. Computed conversion, conversion rate, and glass transition temperature from DSC scan of catalyzed LECy cured at 150 °C for 12 hours, then heated at 2 °C / min.

numerical values of all observed and predicted characteristics, for all of the process and test conditions examined in this paper.) As can be seen in Figure 3, there are indeed three “loss peaks” in the corresponding OTMA scan. It should be emphasized that these three peaks appear not because the sample has multiple T_G values, but because the sample T_G increases as the scan proceeds. Whenever the T_G exceeds the scan temperature, the sample shows high stiffness, whenever the scan temperature exceeds T_G , the sample shows low stiffness, and a peak in the loss and tan delta curves accompanies every switch between high and low stiffness.

The foregoing example vividly illustrates the difficulty in performing dynamic mechanical analysis on thermosetting samples at the recommended, slow heating rates. When the heating

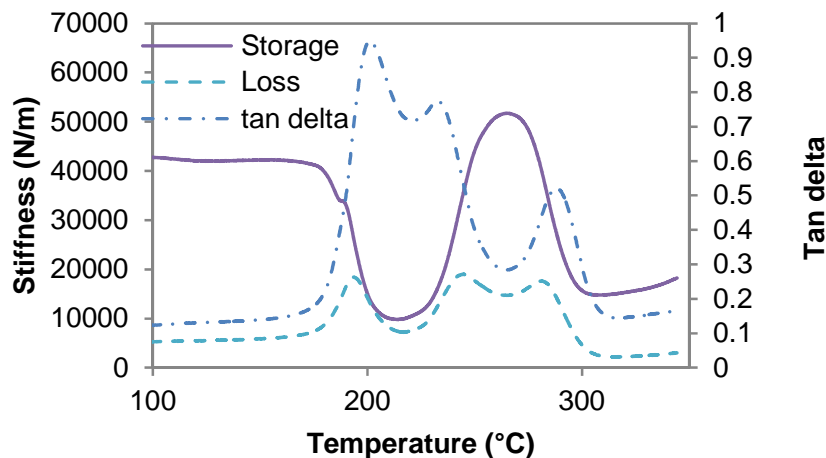


Figure 3. Oscillatory TMA scan of catalyzed LECy cured at 150 °C for 12 hours, then heated at 2 °C / min.

Table 1. Key features of DSC and TMA data for LECy under various cure and test conditions.

Parameter	Case 1	Case 2	Case 3	Case 4
Monomer	LECy	LECy	LECy	LECy
Catalyst Added?	Yes	Yes	Yes	No
Final Cure Temp. (°C)	150	150	210	210
Final Cure Time (h)	12	12	24	24
DSC and OTMA heating rate (°C / min.)	2	10	10	50
Conversion (α), as-cured, DSC	0.882 ± 0.013	0.852 ± 0.017	0.943 ± 0.014	< 0.95
T_G (DSC, as-cured)	164 ± 2 °C	167 ± 2 °C	234 ± 14 °C	250 ± 5 °C
$T_{G\infty}$ (DSC) ^a	270 ± 2 °C	270 ± 2 °C	269 ± 2 °C	n/a
Predicted OTMA loss peaks (°C), low case ^b	159	162	216	n/a
Predicted OTMA loss peaks (°C), medium case ^c	164	167	238	n/a
Predicted OTMA loss peaks (°C), high case ^d	177, 251, 287	181	286	n/a
Observed OTMA loss peaks (°C)	196, 247, 283	178	230	250

^a includes effects of degradation; $T_{G\infty}$ from DSC previously reported as 288 °C

^b assumes conversion at high end of uncertainty range, $T_{G\infty}$ reduced end-of-scan DSC value by degradation during heating, diBendetto parameter λ equals value in the range 0.2 - 0.6 that best fits the DSC T_G , and OTMA loss peak is 5 °C lower than DSC mid-point T_G .

^c assumes conversion at center of uncertainty range, $T_{G\infty}$ at previously reported value, diBendetto parameter λ equals value in the range 0.2 - 0.6 that best fits the DSC T_G , and OTMA loss peak is equal to DSC mid-point T_G .

^d assumes conversion at low end of uncertainty range, $T_{G\infty}$ stays at maximum reported OTMA value during heating (i.e. all degradation happens at or after end of heating scan), diBendetto parameter λ equals value in the range 0.2 - 0.6 that best fits the DSC T_G , and OTMA loss peak is 13 °C high than DSC mid-point T_G .

rate is increased to 10 °C / min., the DSC scan (shown in Figure 4) reveals an exotherm of similar overall energy content, but shifted to a higher temperature. The dynamic plot of conversion, conversion rate, and T_G (Figure 5) shows that, in none of the plausible cases does the T_G catch up to the scan temperature, although in the “high” case it comes close. One might expect that the T_G instability number would be lower for this case due to the faster heating rate, however, is actually higher, at 1.9, because the peak rate of cure is shifted to a higher temperature but remains near the same conversion, resulting in about a six-fold increase in the cure rate. The shift to higher cure temperatures, however, means that the T_G has more “catching

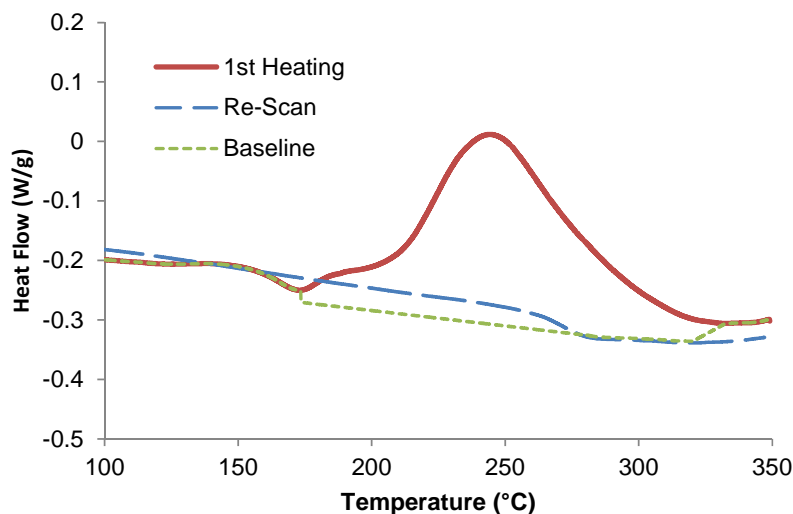


Figure 4. DSC scan of catalyzed LECy cured at 150 °C for 12 hours, then heated at 10 °C / min, showing original heating, re-scan, and baseline.

up” to do, and thus never reaches the scan temperature. The corresponding oscillatory TMA (Figure 6) indeed shows a single T_G at about 180 °C, close to the value seen in the DSC. A careful look at Figure 6, however, reveals a small peak at around 275 °C, accompanied by a continuous increase in the storage component of stiffness. The increase in stiffness is a clear indication that the sample is curing, and therefore that the T_G is changing during measurement, while the small peak may indicate that the T_G comes close to, but does not fully catch up with, the sample temperature.

Figures 7 and 8 shows oscillatory TMA traces for two additional heating rates, 20 °C / min. and 50 °C / min. The single T_G value appears at a temperature that is insensitive to heating rate, a feature that illustrates the effectiveness of the thermal lag determination technique for determining the true “internal” sample temperature, even at very high heating rates. Thus, one of the major issues (thermal conductivity) affecting the reliability of dynamic mechanical scans at high heating rates is easily accounted for, while the issue affecting reliability at low heating rates (*in situ* cure) is much more difficult to manage. It is also worth noting that, even at the higher heating rates, the stiffness of the sample increases over a temperature range that shifts upward as heating rates increase, corresponding very well to the expected effects of residual cure. This upward shift in cure temperature leads to an increase in cure rate, which compensates for the faster heating rate. As a result, *in situ* cure cannot be avoided simply by heating the sample quickly. Instead, in order to observe the true “as cured” T_G , the value of this T_G must be low enough that *in situ* cure is slow compared to the heating rate at the temperature of interest. These facts suggest that, when the T_G is sufficiently high, above about 250 °C for cyanate esters, even the fastest manageable heating rates (which are about 50 °C / min. with the currently available equipment and thermal lag correction techniques) will not be sufficient to provide for a reliable measurement of T_G . In fact, previous work involving blends of the high- T_G cyanate ester PT-30 with LECy have shown that, even at 50 °C / min., the actual “as cured” T_G after curing for 24 hours at 210 °C is not detectable by oscillatory TMA [14].

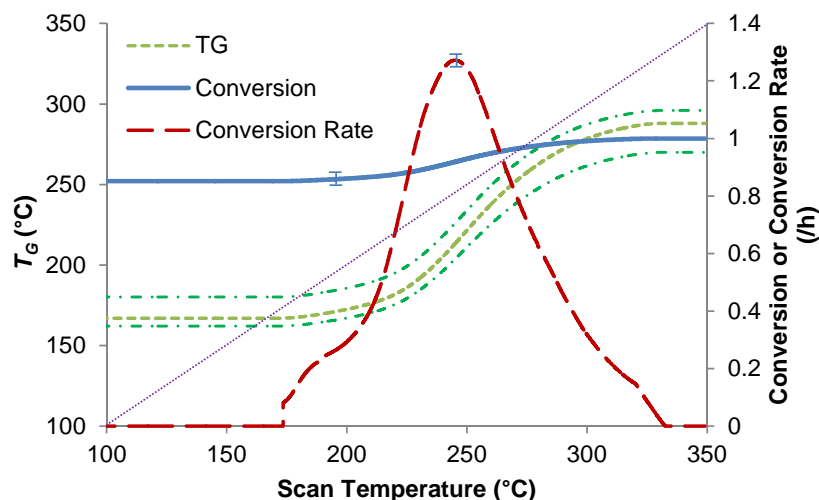


Figure 5. Computed conversion, conversion rate, and glass transition temperature from DSC scan of catalyzed LECy cured at 150 °C for 12 hours, then heated at 10 °C / min.

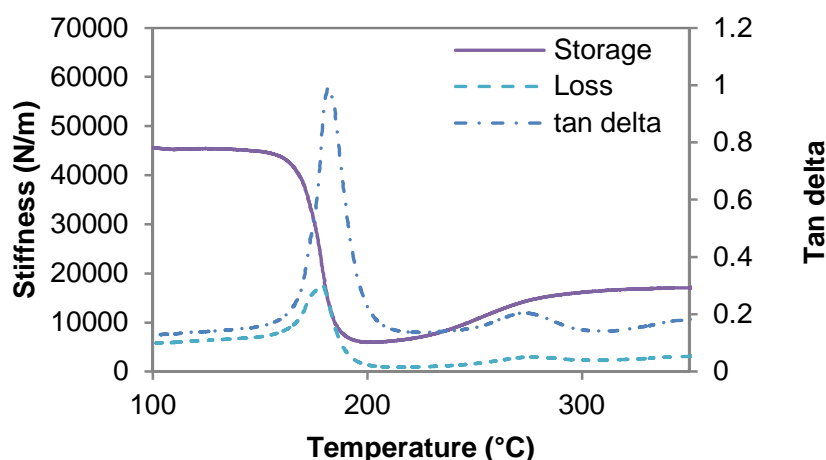


Figure 6. Oscillatory TMA scan of catalyzed LECy cured at 150 °C for 12 hours, then heated at 10 °C / min.

In order to further understand how shifts in residual cure temperature affect the ability to measure T_G values, we examined the behavior of catalyzed LECy cured at a maximum temperature of 210 °C. The DSC data for this sample is shown in Figure 9, with the computed conversion and T_G data in shown in Figure 10. The current algorithm for generating DSC baselines uses a simple step to represent the glass transition in the uncured sample. For samples such as those shown in Figures 1 and 4, where the T_G is already mostly present, the smoothed step does not alter the computed conversion, but it does smooth out the discontinuity near the onset of cure. Also in this case, the measured initial value of T_G is not clearly visible.

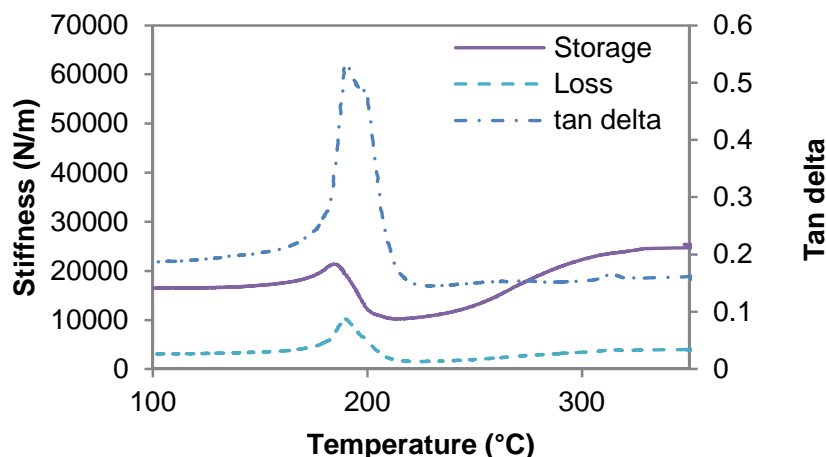


Figure 7. Oscillatory TMA scan of catalyzed LECy cured at 150 °C for 12 hours, then heated at 20 °C / min.

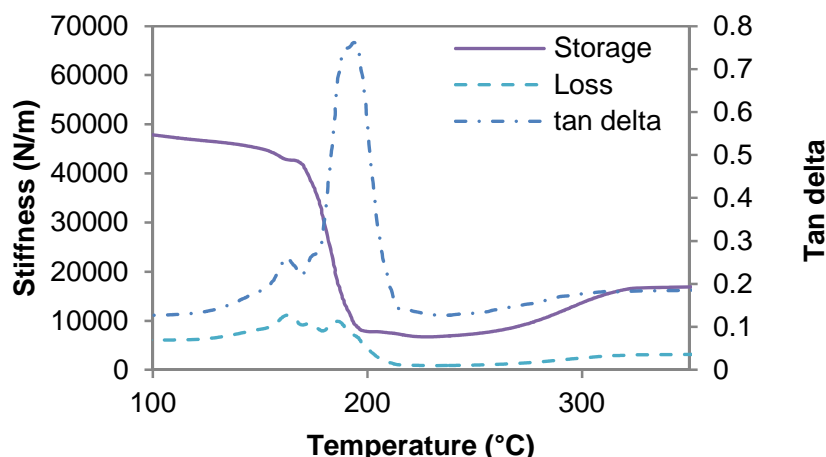


Figure 8. Oscillatory TMA scan of catalyzed LECy cured at 150 °C for 12 hours, then heated at 50 °C / min.

The initial T_G must exceed 220 °C, or otherwise it would appear as a step in the DSC scan. The T_G (by DSC) also cannot exceed about 250 °C, otherwise the very rapid cure observed in the sample would not take place [15]. When this uncertainty is combined with the uncertainty in the DSC to OTMA offset, a very large initial range of T_G is possible. To narrow this range somewhat, we imposed one further condition: the value of the diBenedetto parameter λ should fall between 0.2 and 0.6, a span representing the maximum range of values previously determined in measurements of cyanate esters [4,11-14,16,17].

Figure 10 shows that, in the “race” between the T_G and the scan temperature, the outcome is sensitive to the uncertainties inherent in the data. In the “low” case, *in situ* cure is not significant, while in the “high” case, the sample cures almost completely before a T_G would be seen in an OTMA trace. The T_G instability number for this sample is 0.9, indicating that the rise in T_G should not quite be able to match the scan rate. In the “low” case, there is enough of a lag

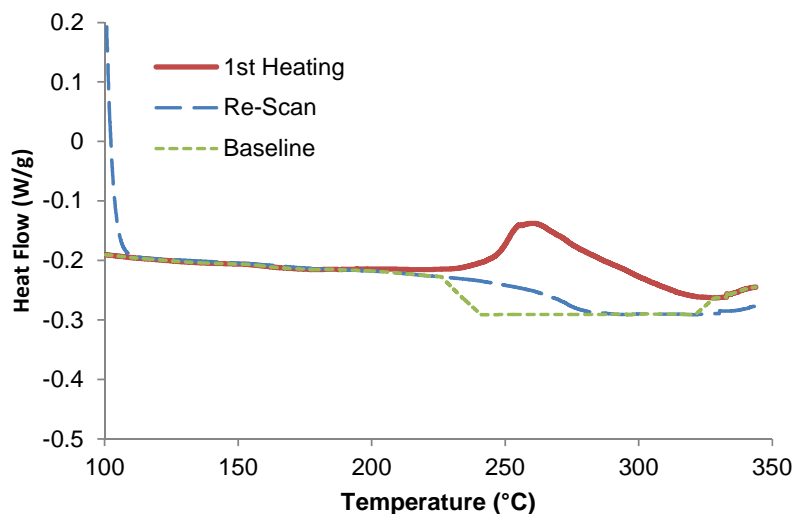


Figure 9. Computed conversion, conversion rate, and glass transition temperature from DSC scan of catalyzed LECy cured at 210 °C for 24 hours, then heated at 10 °C / min.

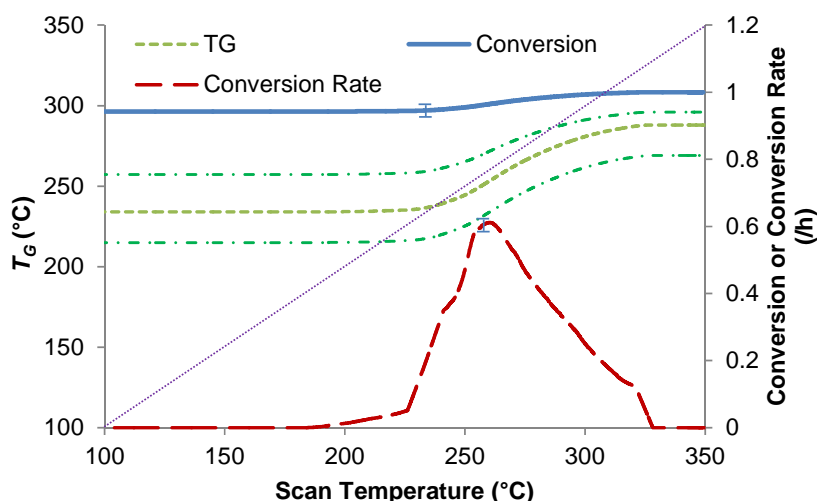


Figure 10. Oscillatory TMA scan of catalyzed LECy cured at 210 °C for 24 hours, then heated at 10 °C / min.

between the glass transition and the start of rapid *in situ* cure that the OTMA measurement is reliable, while in the “high” case, with the initial T_G value being over 250 °C, rapid *in situ* cure starts well before the T_G is encountered.

Figures 11 and 12 show the oscillatory TMA data for the catalyzed LECy cured at 210 °C using heating rates of 10 °C / min. and 20 °C / min., respectively. Only a single T_G is visible in both, however, the 10 °C / min. scan shows a slightly elevated T_G of 230 °C, while the 20 °C / min. scan shows a T_G of 225 °C. Thus, in this case, reliable results were obtained by OTMA, as well as by DSC. However, in previous cases using batches of catalyzed LECy, likely with a greater level of impurities, the OTMA measurements showed T_G values in excess of 280 °C [13,18,19],

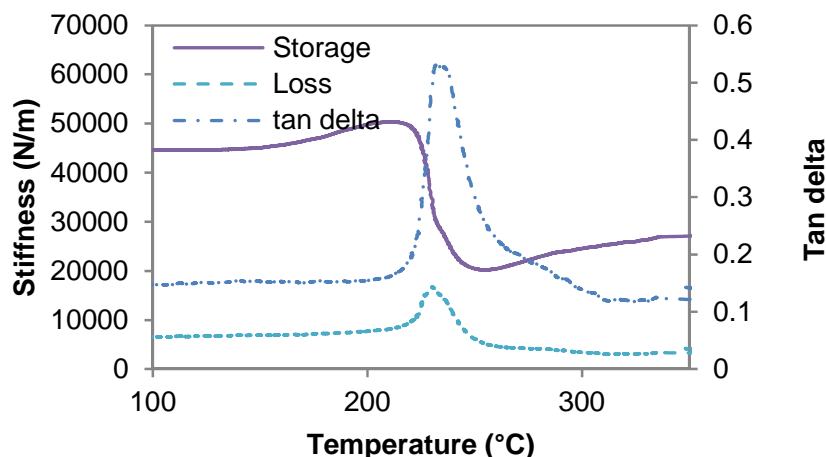


Figure 11. Oscillatory TMA scan of catalyzed LECy cured at 210 °C for 24 hours, then heated at 10 °C / min.

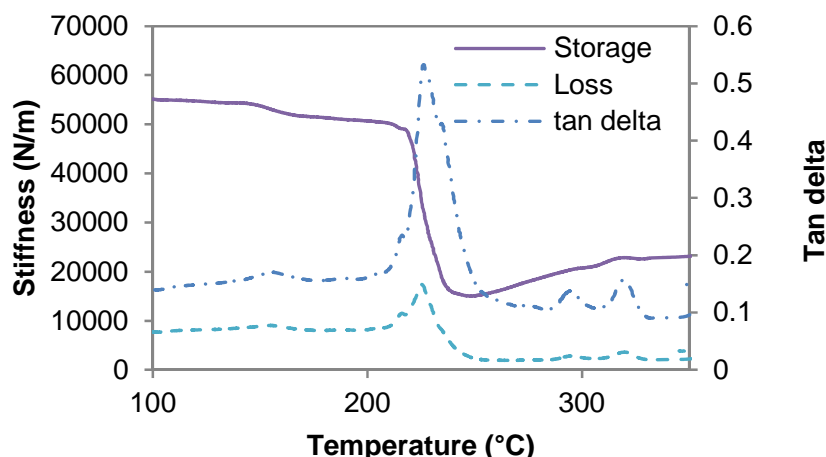


Figure 12. Oscillatory TMA scan of catalyzed LECy cured at 210 °C for 24 hours, then heated at 20 °C / min.

likely reflecting the “high” case shown in Figure 10 in which significant *in situ* cure rendered the measurement unreliable.

In light of these examples, one might wonder if any technique could provide a reliable and precise determination of the T_G value. As reported by us previously [14], DSC scans using a very rapid heating rate of 50 °C appear to provide the needed characteristics. Figure 13 shows the trace for uncatalyzed LECy cured at 210 °C for 24 hours. A clear T_G is visible at 250 °C, and repeated trials showed the value of T_G to be repeatable to within 5 °C for at least three runs. Even when no step change in heat capacity was visible in such scans, the onset of residual cure took place with extreme rapidity, creating a very clear “kink”, rather than a gradual upward curve, in the signal. The corresponding OTMA scan, which also showed a T_G at 250 °C, is shown in Figure 14. Although the loss peak provided a reliable measurement in this case, the tan delta peak is too high by more than 30 °C, and is extremely broad, reflecting significant *in situ*

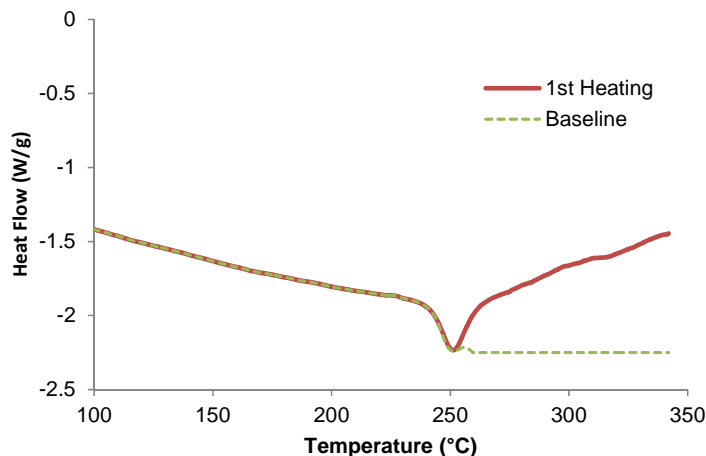


Figure 13. DSC scan of uncatalyzed LECy cured at 210 °C for 24 hours, then heated at 50 °C / min.

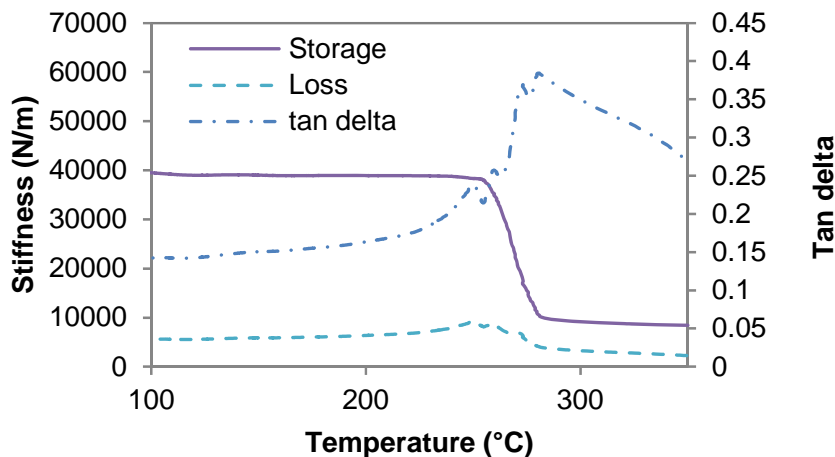


Figure 14. Oscillatory TMA scan of uncatalyzed LECy cured at 210 °C for 24 hours, then heated at 50 °C / min.

cure. In this case, the lack of added catalyst may delay the onset of cure just enough to capture the loss peak and the corresponding drop in stiffness. Because, in this case, the DSC scan provided a clear indication of the “as cured” T_G , the reliability of the OTMA scan can be evaluated even without the need to model the behavior of T_G during the scan. In contrast, an OTMA scan, even one that looks reasonable, may be unreliable, and in order to assess the reliability it is necessary to run a DSC scan, and, at a minimum, to compare the likely range of T_G indicated by the DSC scan with the value measured by OTMA. The same conclusion is likely true for any dynamic mechanical technique, in which a “blindness” to chemistry creates a liability at least comparable to the liability of being “blind” to mechanical properties inherent in a DSC scan.

4. CONCLUSIONS

Using the dicyanate ester of bisphenol E (also known as Primaset LECy), we have illustrated the difficulties inherent in measurement of the glass transition temperature of this high-temperature thermosetting polymer via dynamic mechanical analysis alone. These difficulties all stem from the use of undercured samples, which, somewhat surprisingly, tend to experience significant residual cure when heated past their glass transition temperatures, no matter how rapidly the heating takes place. The fact that a significant chemical reaction is triggered concurrent to the glass transition means that there will always be a “race” between the scan temperature and the evolving glass transition temperature of undercured samples. A reliable measurement of the glass transition temperature by dynamic mechanical analysis is a matter of having the scan temperature “win the race”. It appears that, for cyanate esters, the scan temperature can “win the race” only when the “as cured” T_G is below a critical value. This critical value does appear to depend on factors such as catalysis and heating rate. For samples with an “as cured” T_G above about 250 °C, even a heating rate of 50 °C cannot be considered sufficient to ensure a reliable measurement of the glass transition temperature by dynamic mechanical means alone. In contrast, DSC measurements, particularly those performed at high heating rates, can provide reliable estimates of dry T_G , even when no step change in heat capacity is evident, though the rapid onset of cure triggered by passage through the glass transition.

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